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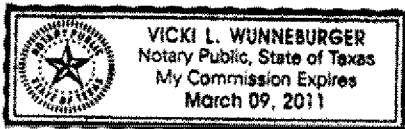
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Subscribed and sworn to before me this 25th day of February, 2008.



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SUPERABSORBER (SUPER ABSORBENT POLYMER "SAP") WITH
BIODEGRADABILITY THAT IS CONSIDERABLY BETTER THAN IN THE PRIOR ART

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Abstract

This invention concerns highly water-absorbent, water-swellable but insoluble products and a method for making them.

Description

This invention concerns new water-absorbent polymers ("superabsorbers"), which can biodegrade rapidly, and a method for producing them.

The term "superabsorber" in chemical technology is understood to mean compounds that are capable of rapidly binding large quantities of water into their structure while forming highly swelling, gel-like bodies.

Although certain cellulose derivatives and other modified natural substances have similar properties, the term superabsorber is preferably used for certain polymer salts and amides of acrylic acids.

Typical representatives of this known group of products are the polymer alkali and ammonium salts of acrylic acid and polyacrylamide, which are obtained by polymerization of the appropriate monomers. They represent the prior art.

To keep these polymers, which are substantially readily soluble in water and aqueous fluids, from passing into solution in the medium that is to be absorbed, small amounts of so-called polyfunctional monomers with the general structure $(CH_2=CR^1)_m-R^2$ are incorporated into the reaction product by polymerization during the polymerization of the monomers. One skilled in the art calls this form of mixed polymerization with the co-use of polyfunctional monomers "crosslinking."

The swelling capacity, and with that, the potential water uptake of superabsorbers produced in this way can be adjusted very precisely through the "degree of crosslinking" (defined by the functionality and amount of polyfunctional monomer incorporated by polymerization).

The stability of the polymers with respect to chemical and biological degradation reactions is inevitably increased with the described crosslinking. However, for many applications, this increase of stability brings considerable disadvantages.

One of the principal areas of use of superabsorbers is, in particular, the hygiene field. Superabsorbers are used in this area as auxiliary agents that are capable of absorbing liquid body secretions rapidly. Typical uses of these products include disposable diapers, in which superabsorbers applied to carrier substances such as nonwovens of cellulose or plastic, can bind to urine through absorption.

The rapid biological degradation of these substances, in order to avoid long-lasting waste products is prevented by the high stability of the products based on the described, more or less highly crosslinked polyacrylates that are used in the prior art as superabsorbers.

The invention according to this claim, therefore, is based on the task of producing superabsorbers that avoid this principal disadvantage of the products known from the prior art without limiting the excellent binding capacity for water that characterizes the superabsorbers based on polymer acrylamides, alkali and ammonium salts of acrylic acids.

This task is solved in accordance with the invention.

The addition of ethylenically unsaturated groups having the general formula $\text{CH}_2 = \text{CR}^1 - \text{R}^2$ to certain natural substances or modified natural substances or compounds such as polyvinyl alcohol by graft reactions is known. Such known reactions are, for example, the insertion of allyl or acryl groups into cellulose, starch or protein molecules. Through the incorporation of the reactive double bond, the doped molecule becomes accessible to copolymerization with other ethylenically unsaturated monomers.

However, it is new and surprising that through the addition of several unsaturated groups to molecules of these natural substances or to polyvinyl alcohol, sufficiently effective (polyfunctional) crosslinkers for superabsorbers can be produced, and these lead to end products that are biologically very readily degradable.

The easy biodegradability of these products in accordance with the claim of the invention is explained by the fact that the base structure of the modified natural substance that is used as crosslinker is practically not changed by the addition of the ethylenically unsaturated groups. Rather, the reactive unsaturated groups are added only in lateral position. The base structure of the described substances that are used for doping, which as anyone skilled in the art knows can be destroyed easily and rapidly by the effect of microorganisms, therefore remains practically unchanged to the attack of these destructive organisms.

The further decomposition of the remaining polymer chains by hydrolysis and the effect of microorganisms becomes considerably easier because of this. This desired extensive degradation of the remaining polymer chains is still additionally improved in the case of the superabsorbers in accordance with the claim of this invention by the fact that, preferably, monomers that contain nitrogen in the form of amine, amide or ammonium groups are used. It is known that compounds that contain these atomic groupings are especially easily accessible to biological degradation reactions.

The polysaccharides can be used as suitable natural substances (or natural substances modified by digestion following methods that are generally known from the literature) for production of crosslinkable reactants for copolymerization with acrylamides or the alkali/ammonium salts of acrylic acid. Preferred natural polysaccharides or natural substances containing them are ones from the group of the poly- α -glycoses like starches, amyloses, amylopectins, dextrans, dextrans and pullulans, from the group of the polygalactoses like gum Arabic, agar, gum tragacanth, carrageenan and pectins, and from the group of the polymannoses like carubin, taragum, algin, alginic acid and guar (galactomannose). Also, polyvinyl alcohol which of course is not classified among the described natural substances, but which is similar to them in many regards, is also expressly mentioned here as being suitable.

Proteins such as gelatins have proven to be particularly suitable modified natural substances for preparation of the crosslinking components of the new superabsorbers in

accordance with the claim of this invention and, therefore, they are especially preferred starting substances for the preparation of crosslinkable reaction products for the monomers necessary to prepare the superabsorbers. Really especially preferred are gelatin hydrolyzates with (low) molecular weights between 100 and 10,000, which preferably can be obtained from gelatins with higher molecular weights by controlled enzymic degradation, as is known to one skilled in the art. The insertion of the reactive, ethylenically unsaturated groups (grafting) onto the molecular structure of the said natural substances, altered or modified natural substances, or to synthetic polymers like the expressly mentioned polyvinyl alcohol takes place by the known reaction of these substances with compounds such as allyl chloride or acryl chloride.

Literature reference: Rauch-Puntigam/Völker, Acrylic and methacrylic compounds [in German], "Springer Publishers, Berlin, 1967; Ullmann (Editor)/R. Köhler, Handbook of Starch, V-1 Starch Glues [in German], Parey Publishers, Berlin, 1971.

Gelatin is accessible to the already described reactions with acryl/allyl chloride not only via the OH groups present in the protein molecule. Reactive acryl groups can be inserted in an especially simple and elegant way into the protein molecule by the reaction of the amino acids present in the protein structure with epoxy acrylates such as acrylic acid glycidyl ester (acrylic acid-2,3-epoxypropyl ester; 2,3-epoxypropyl acrylate). This reaction is also known to one skilled in the art and is not a part of the claim in accordance with the invention. Acryl-derivatized gelatin is especially preferred as crosslinking component of the new superabsorbers according to the claim of this invention, since proteins, as is generally known, are especially easily and rapidly accessible to biological degradation processes.

Another advantage of gelatin derivatized with acryl groups as crosslinker in the new superabsorbers in accordance with the claim of this invention is their simple and rapid copolymerization with the monomers necessary to produce the new superabsorbers, which makes very economical production techniques possible.

For example, it is possible to polymerize the mixture of monomers and crosslinkers within seconds by rapid heating — for example, under the effect of microwaves — or by high energy radiation (electron beam or UV light) and to process the resulting product immediately. These techniques are especially preferred as methods for producing the new superabsorbers according to the claim of this invention.

Application examples

The new superabsorbers according to the claim of this invention and a method for producing them are described in the following examples.

Application Example 1

A reaction product is prepared from 100 parts* acrylic acid and 100 parts aqueous commercial ammonia solution (25%). 22 parts gelatin degraded by hydrolysis and having a molecular weight of about 2000, which had been derivatized with acryl glycidyl ester having 8 $\text{CH}_2=\text{CH-R}$ groups per molecule, in water in the amount of 60%, was dissolved in the resulting ammonium acrylate.

3 parts sodium peroxodisulfate, as initiator, and 1 part triethanolamine, as redox catalyst, were mixed into the mixture, and it was immediately poured into a pan in a film about 5 mm thick and polymerized. The solidified product was dried and ground to a powder with an average particle size of 50 μm .

The resulting superabsorber is characterized by high water capacity with the formation of a stable gel body with significant swelling activity. After storage in simple potting soil (commercial product) the product has practically completely decomposed after only 8 weeks.

Application Example 2

The procedure is carried out as described in Application Example 1. Instead of using the redox catalyst, the mixture is heated for about 240 sec in a microwave apparatus at a power of 2 kW, in which case it polymerizes and is dried to a residual water content of 10%. The product can then be immediately ground.

The resulting superabsorber is characterized by high water capacity with the formation of a stable gel body with significant swelling activity. After storage in simple potting soil (commercial product) the product has practically completely decomposed after only 8 weeks.

Application Example 3

The procedure is carried out as described in Example 1. Instead of the peroxodisulfite about 1% of a commercial water-soluble UV initiator is added to the mixture, the mixture is cast onto an endless belt in an approximately 100 μm thick film and passed under a UV source operating at a wavelength matched to the UV initiator. The transport speed is 3 meters/min. The mixture polymerizes and is then dried to a residual water content of 10% and ground.

The resulting superabsorber is characterized by high water capacity with the formation of a stable gel body with significant swelling activity. After storage in simple potting soil (commercial product) the product has practically completely decomposed after only 8 weeks.

* [Translator's note: parts by weight.]

Application Examples 4-6

The procedure as described in Application Examples 1-3 is carried out, but the ammonia solution is replaced by 70 parts of a 33% NaOH solution in water. The resulting superabsorber of weakly crosslinked sodium polyacrylate is characterized by high water capacity while forming a stable gel body with significant swelling activity. After storage in simple potting soil (commercial product) the product has already clearly degraded after only 8 weeks.

Application Examples 7-9

The procedure is carried out as in Examples 4-6, but the NaOH was replaced by the molar equivalent amount of KOH solution. The result, as was to be expected, corresponded to the results of Application Examples 4-6.

Application Example 10

A mixture is prepared from 200 parts of a 60% solution of acrylamide in water and 25 parts of a hydrolysis-degraded gelatin with molecular weight of about 2000, which was derivatized by the reaction of acryl glycidyl ester having 8 $\text{CH}_2=\text{CH}$ groups per molecule in the amount of 60%, is dissolved [in the mixture].

3 parts sodium peroxodisulfate as initiator, and 1 part triethanolamine as redox catalyst were mixed into the mixture, and the mixture was immediately cast into a pan in an approximately 5 mm thick film and polymerized. The solidified product was dried and ground to a powder with an average particle size of 50 μm .

The resulting superabsorber is characterized by high water capacity with the formation of a stable gel body with significant swelling activity. After storage in simple potting soil (commercial product) the product has practically completely decomposed after only 8 weeks.

Application Examples 11-12

A mixture was prepared as in Application Example 10, and the experiment was carried out as in Examples 2 and 3. The result corresponded to the results as in Examples 2 and 3, as was expected.

Application Example 13

The components of the formulation as in Application Example 1 are continuously dispensed to a reaction device as shown in the drawing in Annex 1 that consists of a tubular body with an internal static mixer, caused to reaction there and immediately discharged with a casting device (slot nozzle) onto a circulating endless belt, where they immediately spontaneously

polymerize. After passing through a drying zone they can immediately be ground to a superabsorber with properties analogous to Application Example 1.

Application Example 14

The components of the formulation according to Application Example 2 are continuously dispensed to a reaction device as shown in the drawing in Annex 2 that consists of a tubular body with an inner static mixer, caused to react there and immediately applied with a casting device (slot nozzle) onto a circulating endless belt, where they polymerize and dry in a microwave field within 240 sec. They can then immediately be ground to a superabsorber with properties analogous to Application Example 2.

Application Example 15

The components of the formulation as in Application Example 3 are continuously dispensed, as shown in the drawing in Annex 3, to a reaction device that essentially consists of a tubular body with an inner static mixer, caused to react there and immediately discharged with a casting device (slot nozzle) onto a circulating endless belt, where they pass through a lighting zone with UV emitters, the wavelength of which is matched to the UV initiator added to the mixture. The transport speed is 3 m/min. The mixture polymerizes and it is then dried to a residual water content of 10% and ground. It can then immediately be ground to a superabsorber with properties analogous to Application Example 3.

These examples are only matters of example for the new products as in the claims of this invention. It will be possible for anyone skilled in the art, by modifying the parameters in accordance with the invention to modify the products described in the examples in diverse ways, by modifying the parameters of the production of superabsorbers in accordance with the invention by copolymerization of acryl amides or alkali/ammonium salts with modified natural substances that are derivatized with ethylenically unsaturated groups and act as crosslinking components and/or make possible rapid degradation of the polymers through their structure, which is readily accessible to biological decomposition reactions.

This applies in particular to the mol ratios of the reactants indicated in the descriptions.

The claim of this invention is expressly also extended to these possible embodiments of the invention as in this claim.

Claims

1. A superabsorber produced by mixed polymerization of alkali or ammonium acrylates of the general formula $\text{CH}_2 = \text{CR}^1 - \text{R}^2$ and/or acrylamide with modified natural substances from the family of the starches, celluloses, proteins derivatized by added ethylenically unsaturated

groups of the general formula $\text{CH}_2=\text{C-R}$, characterized by the fact that the modified natural substances incorporated by polymerization clearly improve the biological degradability of the product resulting from the mixed polymerization or make it at all possible in manageable amounts of time.

2. A superabsorber produced as in Claim 1, characterized by the fact that the modified natural substances doped with ethylenically unsaturated groups have a crosslinking effect through their degree of derivatization (number of ethylenically unsaturated groups per molecule) on the polymer chains of the acrylic acid salts or acrylamides.

3. A superabsorber produced as in Claim 1 and 2, characterized by the fact that protein, preferably gelatin, especially preferably degraded (hydrolyzed) gelatin is used as modified natural substance derivatized with ethylenically unsaturated groups. The molecular weight of the hydrolyzed gelatin can be between 500 and 10,000.

4. A superabsorber produced as in Claim 3, characterized by the fact that the gelatin has been derivatized with 2-40 ethylenically unsaturated groups per molecule.

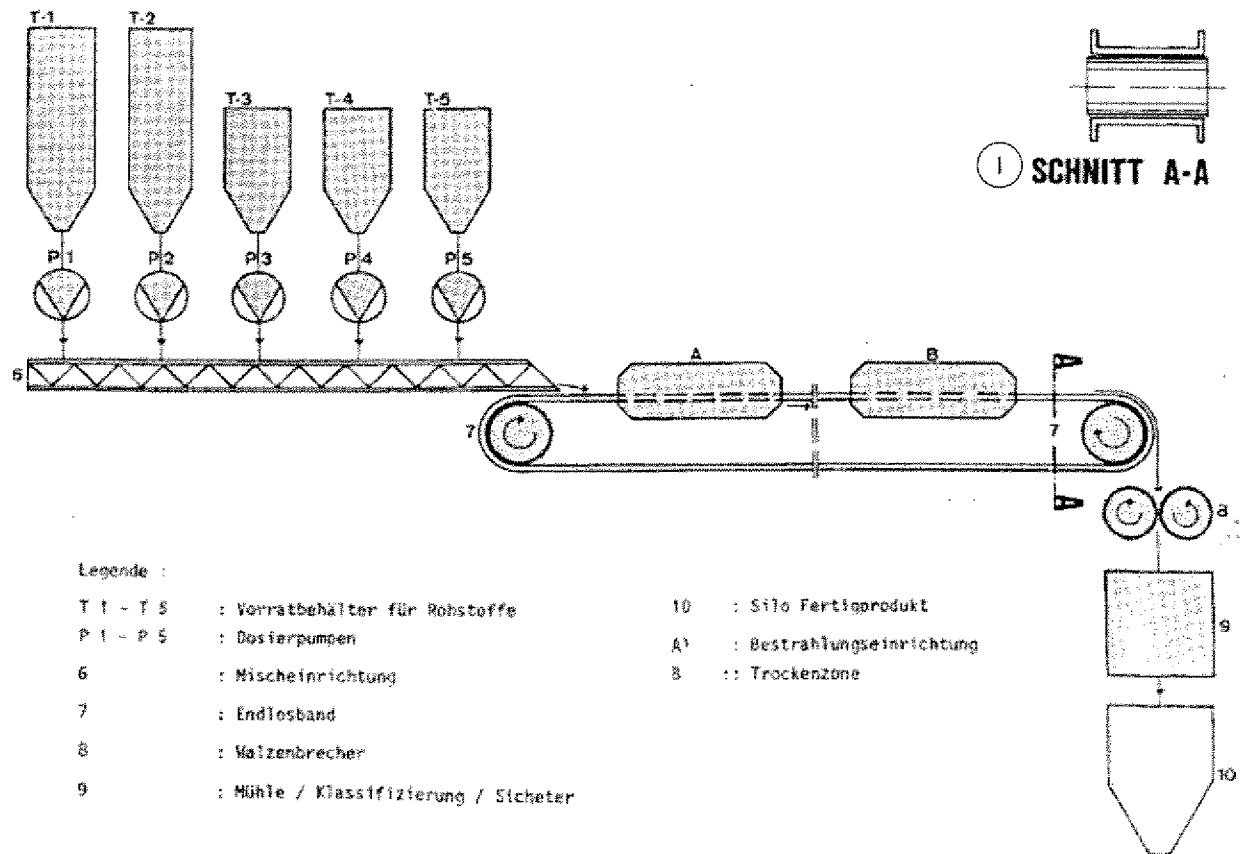
5. A superabsorber produced as in Claims 1-4, characterized by the fact that the said modified natural substances can also be in the form of mixtures of substances.

6. A superabsorber produced as in Claims 1-5, characterized by the fact that the polymerization is initiated by substantially known radical initiators. One may mention as suitable radial initiators azo compounds, peroxides, peroxy compounds and the known initiators for ESH (electron beam hardening) and UV hardening that are known from the literature and accompany documentation may be mentioned as suitable radical initiators.

7. A superabsorber produced as in Claims 1-5, characterized by the fact that the reaction mixture is produced in batches and then polymerized.

8 A superabsorber produced as in Claims 1-5, characterized by the fact that the reaction mixture is produced in a continuous process and then immediately polymerized.

9. A method for producing the superabsorber as in Claim 7 and 8, characterized by the fact that the reaction mixture is applied to an endless belt and [polymerized] by passing through a reaction zone in which energy in the form of radiation acts on the product and through which the polymerization is initiated and optionally the polymer product is already dry. Infrared radiation, UV radiation, microwaves or electron beams (ESH process) can be used as a source of radiation.



Key: 1 Section A-A

Legend:

T1-T5: Supply containers for raw materials
 P1-P5: Dispensing pumps
 6: Mixing device
 7: Endless belt
 8: Roller braker
 9: Mill/classification/screening
 10: Silo for end product
 A¹: Irradiation device
 B: Drying zone